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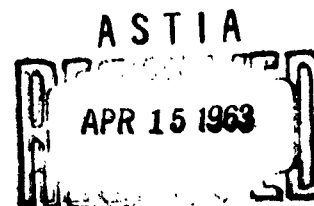
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SPECTROPHOTOMETRIC DETERMINATION
OF THE pKa's OF SOME AROMATIC AMINES

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ABSTRACT

The dissociation constants of the conjugate acids of aniline, α-naphthylamine and β-naphthylamine have been determined from their UV absorption spectra in 50% wt% ethanol-water solution. The values obtained have been compared with potentiometric measurements.

This technical documentary report has been reviewed and is approved.

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TABLE OF CONTENTS

LIST OF TABLES

INTRODUCTORY DISCUSSION

The determination of the pK_a's of the conjugate acids of amines in aqueous solution can be accomplished by potentiometric titration or by spectrophotometric measurements. However, pure water is not a suitable solvent for most aromatic amines. Measurements in non-aqueous or mixed solvent are made difficult because of a lack of suitable hydrogen ion measuring devices. For instance, while a glass electrode will function in alcohol-water solution, the real meaning of the potential is not clearly understood. The use of a spectrophotometric technique eliminates the problem of liquid junction potentials, but in non-aqueous or mixed solvents, the equilibrium laws, in terms of concentration, may be no longer applicable, and only relative dissociation constants for the solvent system will be obtained.

Hammett[1] has investigated the use of several mixed solvents for the determination of the pK_a's of aromatic amines. He used an acidity function defined in (1).

$$H_o = -\log \frac{a_{H^+} \gamma_A}{\gamma_{AH^+}} \tag{1}$$

a_{H^+} is the activity of hydrogen ion, γ_A / γ_{AH^+} is the ratio of the activity coefficients of a neutral base and its conjugate acid. If the ratio γ_A / γ_{AH^+} is the same for all bases, the activity function can be used to calculate pK_a according to (2)

$$pK_a = H_o + \log \left(\frac{[AH^+]}{[A]} \right) \tag{2}$$

Hammett applied H_o to the systems $HClO_4$-H_2O, HNO_3-H_2O, HCl-H_2O, and, most extensively, H_2SO_4-H_2O. The sulfuric acid solutions proved very convenient in use. That medium is, however, most suited to very weak amines. Using amines which lose their color when protonated, Hammett could determine the ratio AH^+/A photometrically. The method was very successful and Hammett has dealt with amines of pK_a 1.11 (p-nitroaniline) to less than -9.29 (2,4,6-trinitroaniline). Stronger bases, such as the naphthylamines, could not be investigated in so strongly protonating a medium.

Elliot and Mason[2] have determined the pK_a's of some aromatic amines in 50% (v/v) ethanol-water at 20°C and 0.2°C. These authors state, "With the aromatic amines the equation $pK_a = pH - \log [B]/[BH^+]$ gave pK_a values with deviations up to 0.1 of a pK unit. Accordingly, the empirical relationships between the stoichiometric hydrogen ion concentration in 50% (v/v) aqueous

1

ethanol at 0.2° and 20.0° and the pH meter reading were determined, and they were used to calculate the classical ionization constants of the conjugate acids of the aromatic amines."

Gutbezahl and Grunwald[3] have used a differential potentiometric technique to measure the pK_a's of some aromatic amines in several compositions of ethanol-water. These authors show that the function H_O does not exist in ethanol-water solutions and the ratio $\gamma_A / \gamma_{AH}+$ is far from constant for all amines. Such closely related amines as aniline and methylaniline showed marked differences in their behavior in ethanol-water solutions of different compositions. Therefore, while it was originally hoped the pK_a's could be determined in terms of activities, expression (3)

$$pK_a = -\log (H^+) + \log \left(\frac{AH^+}{A} \right) \qquad (3)$$

had to be used. These relative dissociation constants determined spectrophotometrically are compared with the potentiometric determinations of Grunwald and Getbezahl[3] and of Elliot and Mason[2].

APPARATUS AND EXPERIMENTAL PROCEDURES

The aniline used was Matheson, Coleman, and Bell reagent grade which had been redistilled to constant refractive index. The α-naphthylamine was from Amend and Company. The β-naphthylamine and 1- and 2-anthryl amines were obtained from Aldrich Chemical Company. Anhydrous reagent grade ethanol and deionized water were used to make up the 50% (wt.) ethanol. Dupont concentrated hydrochloric acid was used. The spectra were obtained on a Cary Model 14 Spectrophotometer with thermostatted cell compartment, held at 25.0 $\pm$ 1°C.

Samples of aniline and α- and β-naphthylamine were weighed and dissolved in 50% by wt. ethanol-water. Because of their very slight solubility, the 1- and 2-anthryl amines were examined as saturated 50% by wt. ethanol-water solutions.

Solutions of the amines were made which were of suitable concentrations for examination of all bands between 215 millimicrons and 400 millimicrons.

In equation (3) AH^+/A is calculated as $\epsilon_{max}-\epsilon/\epsilon-\epsilon_{min}$ for an absorption shown by the amine where ϵ_{max} is the extinction coefficient of the amine in neutral solution, ϵ_{min} is the extinction coefficient in acid solution, and ϵ is the measurement of the extinction coefficient in solutions of intermediate acidity. The reciprocal is used when the absorption is shown by the aminium ion. From this ratio and the total amine (protonated and unprotonated) concentration, the equilibrium concentration of amine and conjugate acid can be calculated. From this and the initial hydrogen ion concentration, the equilibrium hydrogen ion concentration can be calculated.

2

The acid concentrations were determined by potentiometric titration using a saturated calomel electrode and a glass electrode with a silver-silver chloride internal. They are tabulated in Table I.

TABLE I

Determination of Acid Concentrations

Solvent No.	HCl Concentration (moles/liter)
1	0.00
2	$5.160 \cdot 10^{-4}$
3	$9.398 \cdot 10^{-4}$
4	$1.463 \cdot 10^{-3}$
5	$1.829 \cdot 10^{-3}$
6	$3.607 \cdot 10^{-3}$
7	$5.958 \cdot 10^{-3}$
9	$4.691 \cdot 10^{-2}$

To make certain that the aniline was completely unprotonated in neutral solution, an aniline sample was run in $5 \cdot 10^{-3}$ $\underline{N}$ KOH in 50% (wt.) ethanol. The extinction coefficients were identical with those in neutral solution. Similarly, a sample of aniline was run in solvent 9 with 0.05 milliliters of concentrated HCl added to the 50 milliliters of solution. The extinction coefficients were identical with those in solvent 9. In addition, in solvent 9 the 282 millimicron band had completely vanished and there was no peak in the curve at 231.4 millimicrons. The other amines were assumed to have pK_a's within one unit of aniline. The assumption seems well-founded as the peaks used disappeared completely.

RESULTS

Of the five amines examined, only aniline and the naphthyl amines seem to be suitable for examination by the method used. The ideal absorption for this kind of investigation is sharp and approaches zero in the fully protonated state. 1 and 2 anthryl amines are unsuited to this method of analysis because there is an overlapping of the absorption of the amines and ions. At the wavelengths of absorption, there is only a relatively small difference in absorbance between the spectra of the amine and the ion, and it is difficult to find the minimum absorbance for the bands since these minima lie on steeply rising curves. Aniline is very conveniently analyzed using these methods. The amine has two sharp absorption bands at wavelengths where the anilinium ion shows little or no absorption. The ion's absorptions are weak, and fall between the amine's peaks. The naphthyl amines are intermediate between these extremes.

Data for the three lower amines are given in Tables II, III, and IV. For each solution these contain the following information: the ionic strength or initial acid concentration in moles/liter, the initial amine concentration in moles/liter, the wavelength of absorption in angstrom units, the extinction coefficient, the ratio AH^+/A, the equilibrium amine concentration in moles/liter, the equilibrium acid concentration in moles/liter, and the pK_a.

The solutions expected to give most valid results are those having optical densities of about unity, those whose final hydrogen ion concentration is within 30% of their initial value, and those where neither amine nor aminium ion concentration exceeds the other by a great deal.

DISCUSSION OF RESULTS

Aniline was expected to give the most consistent results; however, the various pK_a values are considerably scattered. The mean value, about which most of the values cluster, is 3.99. The four extreme values, 4.23, 4.20, 3.76 and 3.82, tend to minimize each other. Actually, all the values are not of the same precision, and an elaborately weighted mean might be more conclusive.

The data for α- and β-naphthyl amine are much more consistent. The mean values for their pK_a's are 3.25 and 3.58 respectively. The pK_a values of Elliot and Mason[2], and of Grunwald and Gutbezahl[3], are compared with the results of this work in Table V.

From the work of Elliot and Mason[2], the temperature dependence of the pK_a of aromatic amines can be estimated. From the work of Grunwald and Gutbezahl[3], the dependence of the pK_a of aniline on ethanol-water compositions can be obtained. Extrapolating measurements at 25° to 20°C will tend to raise the pK_a; extrapolating to lower ethanol in water composition (50% v/v ethanol-water = 42.5% by weight ethanol-water) also tends to raise the pK_a.

4

If the result of the spectrophotometrically determined value for aniline (pK_a = 3.99) is extrapolated to 20°C and 42.5% by wt. ethanol-water, the value obtained is 4.19, which is in agreement with the value of Elliot and Mason. Similar extrapolations for α- and β-naphthylamine are not possible because of a lack of knowledge of the dependence of their pK_a's on ethanol-water composition.

REFERENCES

1. L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, 1940, Chapter IX.

2. J. J. Elliot and S. F. Mason, $\underline{J}$. $\underline{Chem}$. $\underline{Soc}$., 2353 (1959).

3. B. Gutbezahl and E. Grunwald, $\underline{J}$. $\underline{Am}$. $\underline{Chem}$. $\underline{Soc}$., $\underline{75}$, 563 (1953).

TABLE II

Data for Aniline in 50% by wt. Ethanol-Water

Sol-vent	$\mu \times 10^5$	Initial Conc. Amine x 10^5 M	λ Å	ϵ	$\dfrac{AH^+}{A}$	Eq. ArNH$_2$ Conc. x 10^5	Eq. Acid Conc. x 10^5 M	pK$_a$
#1	-	32.12	2820	1432	-	-	0	-
	-	6.424		1417	-	-		-
	-	25.74		1418	-	-		-
	-	8.582		1404	-	-		-
	-	6.424	2314	8336	-	-		-
	-	8.582		8285	-	-		-
	-	11.12		8336	-	-		-
#2	49.52	42.91	2820	460.3	2.091	13.89	20.6	4.01
	49.80	12.87	2314	194.3	3.356	2.96	41.0	3.91
#3	82.71	128.7	2820	587.4	1.421	53.16	7.2	4.23
	90.24	42.91		227.2	5.37	6.85	54.0	4.00
	90.24	42.91	2314	137.3	5.23	6.89	54.0	3.99
	91.73	25.74		738.2	10.9	2.16	68.2	4.20
#4	128.7	128.7	2820	304.2	3.67	27.5	27.5	4.13
#5	161.0	128.7	2820	215.6	5.60	19.5	51.8	4.03
	178.4	25.7		143.7	8.896	2.6	155.3	3.76
	178.4	25.7	2314	679.9	12.02	1.97	154.7	3.89
#6	317.4	128.7	2820	72.7	18.56	6.58	195.3	3.98
	317.4	128.7	2314	450.7	19.36	6.31	195.0	4.00
#7	572.0	42.91	2820	23.8	43.717	0.72	529.8	3.92
	572.0	42.91	2313	207.4	34.63	0.84	529.9	3.82
#9	-	128.7	2820	0.0	-	-	3999.4	-
	-	128.7	2314	45.8	-	-	3999.4	-

7

TABLE III

Data for α-Naphthylamine in 50% by wt. Ethanol-Water

Sol-vent	μ x 10^{5}M	Initial Amine Conc. x 10^5 M	λ(Å)	ϵ	$\frac{AH^+}{A}$	ArNH$^+_3$ Conc. at Eq. x 10^{5}M	H$^+$ Conc. at Eq. x 10^5 M	pK_a
#1	-	3.099	2410	24,120	-	-	0.0	-
#2	51.17	6.197	2410	14,040	0.810	1.48	49.69	3.21
#3	93.63	3.099	2410	10,490	1.531	1.88	91.75	3.22
#4	145.7	3.099	2410	8229	2.393	2.2	143.5	3.22
#5	181.4	6.197	2410	6850	3.283	2.4	179.0	3.26
#6	357.8	6.197	2410	4276	7.39	2.7	355.1	3.32
#7	591.0	6.197	2410	3340	11.86	2.9	588.1	3.30
#9	-	6.197	2410	1589	-	-	4648.	-

TABLE IV

Data for β-Naphthylamine in 50% by wt. Ethanol-Water

Sol-vent	μ x 10^{5}M	Initial Amine Conc. x 10^5 M	λ(Å)	ϵ	$\frac{AH^+}{A}$	ArNH$^+_3$ Conc. at Eq. x 10^{5}M	H$^+$ Conc. at Eq. x 10^5 M	pK_a
#1	-	0.243	2353	61,925	-	-	0.0	-
#2	51.54	0.135	2353	21,315	2.079	0.1	51.14	3.61
#3	93.24	1.349	2353	15,263	3.461	0.78	92.46	3.57
#5	181.0	1.349	2353	9360	6.934	1.2	179.8	3.59
#6	357.8	1.349	2353	5793	13.98	1.3	356.5	3.59
#7	591.0	1.349	2353	4448	21.54	1.3	589.7	3.56
#9	4654.	1.349	2353	1779	-	-	4653.	-

TABLE V

Comparison of pKa Measurements

	Elliot & Mason[2] Solvent (50% v/v ethanol-water) Temperature		Grunwald & Gutbezahl[3] Solvent (ethanol by wt. % in water) Temperature 25°C			Results of This Work Solvent (50% by wt. ethanol-water) Temperature 25°C
	20°C	.2°C	35%	50%	65%	
Aniline	4.19	4.51	4.161	3.921	3.799	3.99
α-Naphthylamine	3.40	3.72				3.25
β-Naphthylamine	3.77	4.03				3.58

9

Aeronautical Systems Division, Dir/Materials and Processes, Physics Laboratory, Wright-Patterson AFB, Ohio. Rpt No. ASD-TDR-62-1077. SPECTROPHOTOMETRIC DETERMINATION OF THE pK_a's OF SOME AROMATIC AMINES. Final Report, Feb 63, 9 p., incl tables, 3 refs.

Unclassified Report

The dissociation constants of the conjugate acids of aniline, α-naphthylamine and β-naphthylamine have been determined from their ultraviolet absorption spectra in 50 percent by weight ethanol-water solution. The values obtained have been compared with potentiometric measurements.

(over)

1. pK_a
2. Dissociation constants
3. Spectrophotometric analyses
4. Aromatic amines
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